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ALKALINE PROCESS FOR THE MANUFACTURING OF PULP USING ALKALI METABORATE AS BUFFERING ALKALI

The present invention relates to a process for the manufacturing of chemical and semi-chemical pulp from lignocellulosic material.

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Background to the invention

In the last decades, under the driving forces of energy, environmental and economic constraints, large efforts have been made with the aim of finding new technologies to replace the well-established kraft process for the manufacturing of chemical pulp. The traditional kraft process accounts for most of the chemical pulp production in the world and commands
10 several advantages over alternative processes such advantages including insensitivity to wood quality and superior physical pulp properties.

The kraft process however has some well-known drawbacks such as a low pulping yield, generation of odorous reduced sulphur compounds and high capital investments particularly for the chemicals recovery system.

15 Soda anthraquinone (soda AQ) pulping is a well-known process alternative to the kraft process, which offers some simplification of the chemicals recovery process, as there is no requirement for a reducing zone in the recovery furnace. Furthermore the odorous and toxic sulphurous emissions are substantially eliminated by the elimination of sulphide as an active pulping chemical. On the other hand, the replacement of sulphide demands a higher charge of
20 sodium hydroxide to the soda AQ cook in order to compensate for the lost effective alkali from hydrolysis of sodium sulphide in the kraft chemicals recovery cycle. Consequently, the lime reburning and causticising plant in the soda AQ mill, for a given effective alkali charge to the cook, have to be from 20 to 50 % larger than in a kraft mill with a corresponding pulping capacity. Therefore, on balance, and also considering the weaker pulps of traditional
25 soda AQ pulps in comparison to kraft pulps, soda AQ pulping has not met with commercial success and only a few mills in the world are practising the process.

Alkaline pulping processes such as the kraft, soda AQ and alkaline sulphite processes use strong alkali, sodium hydroxide, to provide for the alkalinity of the cook. In the kraft process a chemical reagent referred to as "white liquor" is used for delignification and added to the
30 digester. Typically, the white liquor is an alkaline aqueous solution of sodium hydroxide

(NaOH) and sodium sulfide (Na_2S) containing between about 90 –100 grams/litre of NaOH and about 20-40 grams/litre Na_2S with minor quantities of inert chemicals such as sodium carbonate, sulphate and thiosulphate. Depending upon the wood species used and the desired end product, white liquor is added to the wood chips in sufficient quantity to provide a total charge of alkali of 15-22% NaOH based on the dried weight of the wood.

Typically, the temperature of the wood/liquor mixture in the digester is maintained at about 145°C to 170°C for a total reaction time of about 2-3 hours. When digestion is complete the resulting kraft wood pulp is separated from the spent liquor (black liquor) comprising used chemicals and dissolved lignin.

Conventionally, the black liquor is burnt in a kraft recovery furnace to form a smelt comprising sodium and sulphur chemicals. The smelt is dissolved in an aqueous solution, usually in weak wash, to form green liquor, containing Na_2CO_3 and Na_2S , which is mixed with lime (CaO) to form a turbid mixture containing particles of slaked lime ($\text{Ca}(\text{OH})_2$). The mixture is recausticized according to the scheme



The alkalinity of the liquor is thereby restored and fresh kraft white liquor is obtained for use in the digestion process. The sodium sulphide is not participating in the recausticising process, although sodium sulphide is contributing significantly to the alkalinity of the white liquor. A number of discrete causticizer vessels are normally used to reduce the risk of lime particles migrating directly out of the system without undergoing reaction. Usually, the reacted mixture is passed to a clarifier which separates it into a liquid phase which is strong in NaOH and which is used in the pulping process, and a phase heavy in solids (mainly CaCO_3) which is washed with water to reduce its white liquor content, and then passed to a lime kiln where the solids are calcined to yield fresh CaO . Because of the inefficiency of the conventional recausticizing process, a dead load of unreacted Na_2CO_3 , considered as an inert in alkaline cooks such as kraft and soda AQ, is carried in the white liquor to the pulping process and hence through the kraft liquor cycle. The white liquor content of strong alkali, all of NaOH and one half of the Na_2S content is called effective alkali.

In soda AQ pulp mills the recausticising and lime reburning operation is essentially the same as in the kraft process except that, for a given charge of effective alkali, even larger

equipment capacities are needed for the regeneration of strong alkali as there is no contribution of effective alkali from sodium sulphide hydrolysis.

The causticising and lime reburning operation in pulp mills represent a high investment and operating cost and frequently these units are bottlenecks in mill expansion projects.

5 Over time there has been a considerable interest in finding ways to eliminate the lime reburning and causticising operation in alkaline processes through so called autocausticising. The proposed autocausticising processes are normally based on the use of amphoteric salts to release carbon dioxide directly from sodium carbonate in the kraft recovery furnace. Strong alkali (NaOH) is then generated directly from the smelt in a dissolving tank. The most
10 promising autocausticising agents are based on boron. Boron based autocausticising could potentially supply either part or all of the hydroxide requirements in the kraft pulping process. Janson initiated the use of borates for autocausticising in the pulp and paper industry in 1976 and a US patent was granted to Janson in 1977, US Pat No 4,116,759. A full-scale mill trial on Janson's autocausticising concept was performed at the Enzo Gutzeit linerboard kraft mill
15 in Kotka, Finland in 1982. The results were inconclusive and the mill discontinued the use of borates for autocausticisation. Due to the high load of boron compounds in the pulping liquor, in accordance with the stoichiometry proposed by Janson, the ionic strength of the borate liquor was much higher than the corresponding kraft pulping liquor. Increased ionic strength of the cooking liquor is commonly said to have a negative impact on the rate of
20 delignification. Furthermore, the large boron charges significantly increased the inorganic load in the recovery cycle.

In their research, Janson and co-workers concluded that the presence of sulphide in the recovery boiler smelts counteracts the autocausticising reactions of borates, which would be an obvious drawback in kraft applications. Moreover, for sulphide containing smelts, the
25 presence of carbon dioxide exacerbated the negative effect of sulphide. (J. Jansson, Paperi ja Puu No 8, 1979, 495-504.) In the binary smelt system ($\text{Na}_2\text{S} - \text{B}_2\text{O}_3$), glass formation has been found to occur and compounds of the structure $\text{Na}_2\text{S} \cdot n\text{B}_2\text{O}_3$ ($n = 2-4$) are formed. Thus any sulphide present in the recovery boiler smelt would bind to borates, which else would be available for autocausticising reactions. Indeed more recent mill scale borate autocausticising
30 trials in kraft mills have indicated lower than expected autocausticising efficiency, which may, at least partly, be due to the presence of sulphide.

Janson concluded that, of the different borates, sodium metaborate (NaBO_2) was too weakly alkaline to be considered for pulping, but quite possible to use in e.g. oxygen bleaching applications. (Janson, J., Paperi ja Puu - Papper och Trä, No. 8, 1979, 495-504). In his '759 patent Janson teaches, " if the borate in its causticised form is sufficiently alkaline which is the case for secondary sodium borate Na_2HBO_3 , it is useable as delignification chemical. Oxygen bleaching experiments are presented in '759 as examples of the use of the weaker alkali NaH_2BO_3 . Janson as well as other researchers in more recent borate pulping studies indeed treats the sodium metaborate as an inert during pulping and after the strong hydroxide is consumed in the borate liquor cooks the boron is present as metaborate in the spent pulping liquor.

Of the borates studied by Janson the strongly alkaline tetrasodium diborate ($\text{Na}_4\text{B}_2\text{O}_5$), or (Na_2HBO_3) in aqueous solutions, were selected as the source of alkali and this latter substance was used in pulping experiments. The tetrasodium diborate stoichiometry of Janson suggests the presence of one mole of boron compound (as boron) for every mole of regenerated hydroxide in the pulping liquor. After the digestion process, the borate containing spent pulping liquor comprises dissolved lignin and borate corresponding to the composition of (NaBO_2), sodium metaborate. The spent liquor is burned in a recovery furnace and the tetrasodium borate is formed to complete the autocausticising cycle of Janson.

Janson also briefly discussed the use of anthraquinone in combination with hydroxide or disodium borate (Na_2HBO_3) as alkali source. It was, however, concluded that the hydroxide based cooks proceeded considerably faster, especially in the early phase, than the borate based cooks. (Janson, J., Paperi ja Puu - Papper och Trä, No. 8, 1979, 495-504)

Further work in the area of autocausticising were performed by Wandelt and co-workers during the 1990ties trying to establish whether borate based autocausticising pulping liquors were as good as sodium hydroxide based cooking liquors in terms of delignification rate, selectivity of delignification, and the quality of the final pulp. The gravity of work by Wandelt and co-workers were on kraft applications, in other words for pulping systems comprising sulphide, but data were also reported for soda AQ borate alkali pulping experiments. Disodium borate (Na_2HBO_3) was used as borate alkali. They concluded that "a very slow delignification rate was obtained for sulphur-free soda AQ borate cooking, where instead of 19.5 % NaOH (originating from hydrolysis of the Na_2HBO_3) on wood, 26.7 % NaOH had to be used to achieve kappa number 60 during 90 minutes of digestion at 170°C , and it was

practically impossible to get bleachable grade pulp of kappa No. 30. Such a process cannot compete with conventional pulping." (Prihoda, Wandelt, Kubes, Paperi ja Puu - PAPER AND TIMBER, Vol 78, No 8, 1996 p 456-460.)

In these prior art borate pulping studies the sodium to boron molar ratio in circulating liquors was kept well below 2 and indeed, Janson in US Pat No. 4,111,759 teaches that it is essential to keep the sodium to boron molar ratio equal to or less than 2 in order to ensure desired autocausticisation. Sodium carbonate (Na_2CO_3), commonly considered as an inert component in a kraft pulping liquor will be present in typical recovery boiler smelts and, if autocausticisation is not 100 % efficient, this compound will also be present in the pulping liquor. Sodium carbonate however was not added to any of the borate pulping liquors used in the above referenced pulping studies.

There are recent indications that a key borate compound formed in a recovery furnace would be trisodiumborate (Na_3BO_3), rather than the tetrasodium borate ($\text{Na}_4\text{B}_2\text{O}_5$) as suggested by Janson. This has sparked a new wave of interest in borat-based autocausticising. Trisodium metaborate will form strong alkali and sodium metaborate upon dissolution in water. The overall stoichiometry suggests that only half a mole of borate is needed to regenerate one mole of hydroxide in the liquor system. Two patents have recently been issued in USA using borates for partial autocaustising combined with traditional lime causticising, US Pat No. 6,294,048 and US Pat No. 6,348,128. Both these patens are based on the use of lime and conventional causticising to prepare strongly alkaline pulping liquor.

The phase equilibrium diagram of the binary system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ shows the existence of the compound trisodiumborate at molar ratios of sodium to boron over about 3:1. Janson suggested that trisodiumborate would not form in the sodium boron smelts because of the strongly basic character of the B_2O_5 ion but it has been shown experimentally that at least a portion of trisodium borate is formed by reacting borates in excess sodium carbonate at high temperatures. There is, however, evidence on a poor conversion efficiency of reactants to form trisodiumborate in sodium carbonate- borate smelts for example in the body of US Pat 2,146,093 ". Method of producing caustic borate products". A high reaction temperature, at least 1050°C is needed to obtain trisodiumborate from the reactants and as high as 50 molar percent of the carbonate reactant is still left unreacted in the smelt (Fig 3 and appended text to fig 3 in US Pat 2,146,093). More recently it has been shown experimentally that the

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As referred to above, pulping liquors based on sodium metaborate with or without the presence of sodium carbonate have hitherto not been considered appropriate for use in alkaline pulping processes.

5 In the laboratories of the inventor of the present invention new discoveries have been made relating to sulfur chemicals free pulping and a new process named the NovaCellTM process is being tested in mill scale in central Europe. The new process is partly described in PCT/SE00/00288, published as WO 00/47812. Although WO 00/47812 describes a process with several advantages relative to the traditional kraft process, the capital and operating costs for causticising and lime reburning is quite considerable for certain applications and wood
10 raw materials.

The major objective of the present invention is to provide an alkaline process for the manufacturing of pulp from lignocellulosic material wherein alkali metaborate is providing alkalinity and buffering capacity during delignification. At least a portion of the alkali used for delignification is recovered from the chemicals recovery cycle in the mill without prior
15 reactions with lime for generation of strong alkali. Other objectives such as elimination of odorous compounds by replacing sulphide with quinone catalysts will be further described in the detailed description and appended claims.

Summary of the invention

The present invention concerns a new environmentally sound, capital and cost-effective
20 process for the manufacturing of chemical and semi-chemical pulp from lignocellulosic material. The process uses alkaline pulping liquors comprising dissolved alkali metaborate and alkali carbonate as major alkaline components providing alkalinity and buffering capacity during delignification. The alkaline components of the pulping liquor are recovered from a chemicals recovery furnace and at least a portion of the alkali is recycled and used for
25 delignification without any prior reactions with lime for generation of alkali hydroxide. A quinone based delignification catalyst may be added to be present during delignification. In a preferred embodiment of the invention the quinone pulping catalyst is added prior to alkaline delignification, said delignification conducted in the substantial absence of sulphide.

Short description of the drawings

The invention will be described in closer detail in the following description, with reference to the attached drawings, in which:

Figure 1 is a diagram showing pulp yield as a function of kappa number for softwood (*Picea abies*) for a process according to the present invention, the Soda-AQ, and the Kraft process. Solid lines correspond to cooking and dotted lines to oxygen delignification and bleaching.

Figure 2 is a diagram showing the reject yield as a function of kappa number for softwood (*Picea abies*) for a process according to the present invention, the Soda-AQ, and the Kraft process.

Detailed description of the invention

Laboratory studies performed by the present inventor have shown that a mild prehydrolysis pre-treatment (hydrothermolysis) of softwood material (*Picea abies*) in the presence of a delignification catalyst, primarily anthraquinone (AQ) or its derivatives, improves the cooking results significantly compared to the traditional soda AQ cooking. The application of AQ in a slightly acidic environment prior to cooking has shown surprising effects on the delignification selectivity, which is quite contradictory to common experience and practise, wherein AQ is added in a strongly alkaline environment. Now it has been discovered that the appropriate application of quinone based catalysts combined with delignification using alkaline solutions comprising sodium metaborate (NaBO_2) and (Na_2CO_3) as major components can efficiently delignify lignocellulosic material and that the rate of delignification is considerably improved relative to prior art borate pulping schemes. These discoveries opens up for a complete elimination of the causticising and lime reburning operation in alkaline pulp mills and enable a conversion from kraft to a sulphur free process in existing mills with a minimum of capital expenditure. New pulp mills can be erected without installation of causticising, lime reburning and odorous gases treatment plants.

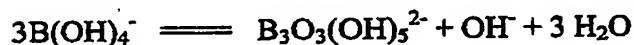
The fibreline of the softwood or hardwood mill practising the present invention thus comprises a wood size reduction step providing a stream of finely divided lignocellulosic material followed by a wood pre-treatment stage wherein the lignocellulosic material is subjected to hydrothermolysis by the action of steam or heat treatment in a hot aqueous solution. The hydrothermolysis is conducted in period of from about 2 to 200 min in a

temperature range of 90-150 C. Excess liquor may be withdrawn from the pre-treatment stage, such liquor having a pH below 7 and comprising organic acids and dissolved metal ions such as Ca and Mn ions. An organic or inorganic delignification catalyst is added to or after the hydrothermolysis stage such catalyst being present in a subsequent delignification stage. The hydrothermolysis impregnation step is followed by alkaline delignification in an aqueous buffer alkali solution comprising alkali metaborate and alkali carbonate as major components.

The metaborate and carbonate is thus providing a buffering effect during delignification in the present invention. The mechanism is not fully clear but it is known that the conjugate base of monomeric boric acid in aqueous systems is the tetrahydroxyborate anion or metaborate anion B(OH)_4^- . The metaborate anion is the predominant specie at higher pH in alkali metaborate solutions while polyboric species are supposedly present at lower pH in accordance with;



and



Thus in metaborate anion containing buffer solutions, fresh hydroxyl ions may be formed and used for dissolving lignin.

The alkali metaborate containing liquor of the present invention is thus providing buffering capacity during delignification in a pH range between 11 and 13. Synergistic buffering effects may be obtained with the carbonate ions also present in the pulping liquor.

The aqueous buffer alkali may contain other compounds but as these components either are inert and undesirable or formed by dissolution of higher borates which, as discussed above, are recovered in rather low yields and only under ideal conditions at high temperature in a recovery boiler smelt, the combined concentration of alkali metaborate and sodium carbonate in the pulping liquor of the present invention is kept higher than the combined concentration of other components.

The concentration of metaborate or metaborate ions in the buffering solution relative to the combined sodium and potassium content of the solution should be kept within a certain range. An upper limit is set to avoid formation of excessive amounts of inert higher borates such as borax in the recovery smelt and a lower limit set to provide a meaningful concentration of

metaborate or metaborate ions in the buffering solution. Thus the metaborate and metaborate ions should be present in an amount providing a sodium plus potassium to boron $((Na + K)/B)$ molar ratio in the alkaline buffer solution in the range from about 1:1 to about 10:1. Preferably the range is kept between 1,5:1 and 5:1 and yet more preferable in the range of 1,5:1 to 4:1.

The requirement of boron compounds for obtaining the desired concentration of metaborate or metaborate ions in the alkaline buffer can be provided, for example, by the addition of a boron compound such as boric acid or an alkali borate to the spent pulping liquor.

The delignification is allowed to proceed until a lignin content corresponding to kappa numbers ranging from about 20 to 120 for softwood pulp qualities and from about 15 -100 for hardwood pulp qualities is obtained. For the manufacturing of bleached pulp qualities, cooking may be followed by extended oxygen delignification using metaborate/carbonate alkali as alkali source and final bleaching to the desired brightness in TCF or ECF sequences. The metaborate alkali could be used, with or without addition of strong alkali, to provide alkalinity in alkaline bleaching stages including peroxide bleaching stages.

Recovery of energy and chemicals is an essential feature of any modern pulping process. The spent pulping liquor from the alkaline pulping process of the present invention, the metaborate black liquor, is extracted from the digester and transferred to an evaporation plant. After concentration the black liquor is burned in a recovery boiler or fully or partially oxidised in a gas generator for recovery of energy and chemicals. The inorganic ash or smelt is recovered and mixed with an aqueous solution to form new raw cooking liquor. Non-process elements are removed and the fresh metaborate containing cooking liquor is recycled to the fibreline to complete the cycle.

It should be recognised that the alkali borate to a great extent is dissociated in (Me^+) , $B(OH)_4^-$ and polyboric anions in the pulping liquor but for convenience, and as is common practise in the pulping industry, the pulping liquor components are expressed as $(NaBO_2)$ (sodium metaborate), $(NaOH)$ or (Na_2CO_3) rather than as ions in solutions. (Me^+) is a sodium or potassium cat ion.

Strong alkali in the form of hydroxide ions may also be present in the pulping liquor, such as hydroxide ions originating from any alkalisulphide, disodiumborate or trisodiumborate

components formed in the furnace smelt, which components upon dissolution will form hydroxide ions.

Typical concentration ranges of the components in the pulping liquor of the present invention are as follows;

5	NaBO ₂	25 - 150 gram/litre (polyborates calculated as NaBO ₂)
	Na ₂ CO ₃	25 - 100 gram/litre
	NaOH	0 - 50 gram/litre
	Na ₂ S	0 - 40 gram/litre
	NaBO ₂ + Na ₂ CO ₃	80-200 gram/litre and > NaOH+Na ₂ S
10	Total alkali	100 - 200 gram/litre

The charge of total alkali on wood needed in order to obtain the desired degree of delignification will vary with wood species and product specifications, but is in the order of 100 - 300 kg chemicals on dry wood for chemical pulps and 40 - 150 kg for the preparation of semi chemical pulps.

- 15 Some initial laboratory experiments have been performed and as shown in figure 1 the pulp yield obtained by the new process may be significantly higher at a given kappa number compared to conventional Kraft cooking. The yield gain at kappa number 60 is 3 - 4 % on wood compared to the conventional Kraft process and 1 % higher compared to the traditional soda AQ process. In addition the fibre defibrillation point in the new process is moved
- 20 towards higher kappa numbers (lignin contents), figure 2. When producing pulps of bleachable grades the cook can thus be terminated at high kappa numbers prior to oxygen delignification without inter-stage mechanical refining. This cooking schedule will support a higher overall pulp yield and furthermore, shorter cooking time in the digester is required. The preliminary laboratory results indicate that the fully bleached pulp can be obtained in 3 -
- 25 4 % higher pulp yield compared to Kraft pulp. This corresponds to a wood saving in the order of 6 - 8 % at a given production rate or an increased capacity of 6-8 % at a given wood consumption.

The high fibre defibrillation point obtained in the new process enables the production of high yield pulps for sack and liner qualities without on-line refining. Energy savings in the order of

30 300 kWh/ton of pulp as well as pulp quality improvement (due to less mechanical damage) can be expected. As shown in figure 1, the yield gain at kappa number 80 is approximately 4

% on wood compared to Kraft process. Another interpretation and/or route to exploit the yield gain may be that at a given pulp yield the lignin content in pulp can be reduced while the carbohydrate content is increased, translating to a greater flexibility in tailoring the fibre properties.

5 It has been suggested that in alkaline environment quinone based pulping catalysts such as AQ work in a redox-pair with anthrahydroquinone, AHQ. In this reaction, AQ stabilises the carbohydrates by oxidising their reducing end-groups to more alkali-stable aldonic acid groups while AQ itself is reduced to AHQ. The AHQ formed reacts with the lignin, which is fragmented, while AHQ is oxidised back to AQ. The efficiency of anthraquinone, added prior
10 to and present in an alkaline delignification stage wherein metaborate and carbonate ions are major components, is quite surprising, and the mechanisms involved are not clear to us. Earlier work clearly indicated a negative influence of borate on the rate of delignification and it was proposed that the retardation of borate pulping was due to a substantial delay in the start of the bulk delignification stage. (Prihoda, Wandelt, Kubes, Paperi ja Puu – PAPER
15 AND TIMBER, Vol 78, No 8, 1996, p 459). Furthermore, an increase in ionic strength of the pulping liquor is claimed to retard the rate of delignification in conventional alkaline processes. A pre impregnation zone or hydrothermolyis stage wherein a quinone additive is added prior to an alkaline pulping stage, as in a preferred embodiment of the present invention, seems to negate the delay of the bulk impregnation stage in sulphide free borate
20 pulping schemes.

Treatment of wood chips with steam or water of up to 200°C has been practised commercially as a first stage in the manufacture of dissolving pulps, where the objective is to remove the hemicellulose while preserving the alfa-cellulose. Operation of a mild prehydrolysis stage (hydrothermolysis) at a temperature below 140°C, preserving a larger portion of the
25 carbohydrates, followed by an alkaline delignification stage, enable the production of a chemical pulp in higher yield with preserved fibre strength properties. A requirement is that lignin self-condensation reactions are suppressed during hydrothermolysis. Our present hypothesis is that anthraquinone may have a dual function in the new process, as a lignin condensation prevention or lignin-carbohydrate bond breaker additive active during
30 hydrothermolysis and as a delignification catalyst, protecting carbohydrates from excessive peeling and supporting delignification in the subsequent metaborate alkaline cooking stage. The latter function is not inhibited as a consequence of the presence of borate ions; on the

contrary, due to the buffering capacity of metaborate and/or other effects the rate of delignification is increased, in spite of a higher ionic strength.

While the description herein largely relates to the use of sodium as alkalimetal base, potassium and sodium/potassium mixtures may be the preferred alkali metal bases in mill scale applications. It can be noted that $K(BO_2)$ or potassium metaborate, have a stronger alkaline reaction in solution, buffering at higher pH than sodium metaborate and thus could be an even better base, particularly for pulping pine and other softwoods. Potassium metaborate would be formed directly in the smelt of a recovery furnace. Higher potassium borates, di and tri potassium monoborate, are only sparsely reported in literature but whether these compounds, which would yield a strongly alkaline reaction, would form in a recovery furnace is unclear.

The method of the present invention can be practised and introduced in existing kraft or soda mills and can be used for making chemical, high-yield and semi chemical pulps from both hardwoods and softwood. While an important feature of the present invention is the potential to replace the sulphides used in the kraft pulping process, some sulphur will always enter the liquor cycles and the sulphidity of the pulping liquor may therefore increase. A sulphide concentration level of below 5 grams/litre in the pulping liquor is desirable in a "non-sulfur" pulp mill and various forms of sulphur purge from the liquor or ash handling system should be explored.

Accordingly, various modifications and changes of the invention can be made and, to the extent that such variations incorporate the spirit of this invention, they are intended to be included within the scope of the appended claims.

Claims

1. An alkaline process for the production of a pulp from lignocellulosic material and the recovery of pulping chemicals used in said process comprising the steps of:

- a) providing a feed stream of finely divided lignocellulosic material,
- 5 b) contacting lignocellulosic material in a digester with an alkaline aqueous buffer solution comprising at least one of a sodium or potassium compound and a boron compound, during a period of time and at a temperature sufficient to obtain a stream of substantially delignified lignocellulosic material,
- 10 c) further treating said substantially delignified lignocellulosic material to obtain a pulp product,
- d) extracting spent liquor comprising dissolved lignin components and spent chemical substances from step b),
- e) partly or fully oxidizing spent liquor originating from step d) in a recovery boiler or gas generator providing one gaseous stream comprising carbon dioxide and one solid or liquid ash stream comprising at least one of a sodium
15 or potassium compound and a boron compound.

wherein

- 20 i) a boron compound in the alkaline buffer solution in step b) is a metaborate or tetrahydroxy metaborate ion, $B(OH)_4^-$, originating from the dissolution of alkali borates in an aqueous liquid, said metaborate and metaborate ion being present in an amount providing a sodium plus potassium to boron $((Na + K)/B)$ molar ratio in the alkaline buffer solution in the range from about 1:1 to about 10:1.
- 25 ii) the solid or liquid ash stream comprising sodium or potassium compounds and boron compounds provided in step e) is dissolved in an aqueous solution to provide an alkaline buffer solution comprising metaborate and carbonate ions, whereof at least a portion is transferred to step b) or c) without prior subjection to treatment with lime or calcium compounds for the generation of hydroxide ions.

iii) the solid or liquid ash stream in e) comprises alkali metaborate and alkali carbonate, which substances, or corresponding ions after dissolution of the solid or liquid ash stream in an aqueous solution, are present in a combined concentration which is higher than the combined concentration of other dissolved compounds originating from dissolution of said solid or liquid ash stream in the aqueous solution.

2. The process according to claim 1 wherein the finely divided lignocellulosic material provided in step a) is subjected to a pre-treatment before contact with the alkaline buffer solution in step b)
3. The process according to claim 2 wherein the pre-treatment includes a mild prehydrolysis step wherein the lignocellulosic is submerged in a hot aqueous solution or heat treated by the action of steam or both.
4. The process according to any of the preceding claims wherein a delignification catalyst is added to be present in step b) of claim 1.
5. The process according to claim 3 and 4 wherein a delignification catalyst is added to the lignocellulosic material and present during the mild prehydrolysis step.
6. The process according to claim 1, wherein the concentration of sulphides in an aqueous alkaline buffer solution is lower than about 5 grams/litre.
7. The process according to claim 1, wherein further treating said substantially delignified lignocellulosic material to obtain a pulp product in c) comprises at least one of an alkaline oxygen delignification or an alkaline bleaching stage.
8. The process according to claim 7, wherein at least a major portion of alkaline buffer solution used in an oxygen delignification or bleaching stage is recycled from a chemicals recovery system without prior subjection to treatment with lime or calcium compounds for the generation of hydroxide
9. The process according to claim 1, wherein at least a major portion of the alkaline buffer solution used in step b) is recycled from a chemicals recovery system without prior subjection to treatment with lime or calcium compounds for the generation of hydroxide.

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10. The process according to any preceding claim wherein a chemicals recovery system for recovery and preparation of alkaline buffer solution used in step b) does not include a limekiln or causticising plant for regeneration of pulping chemicals.
11. The process according to any of the preceding claims, wherein said delignification catalyst
5 is selected from aromatic organic compounds, preferably anthraquinone or a derivative of anthraquinone and added in a quantity ranging from 0.05 % to 0.5 % on dry lignocellulosic material.
12. The process according to any of the preceding claims wherein said delignification catalyst is a sulphide.
- 10 13. The process according to claim 1 wherein a boron compound in the alkaline buffer solution in step b) is present in an amount providing a sodium plus potassium to boron ((Na + K)/B) molar ratio in the alkaline buffer solution in the range of from about 1.5 to about 5, and yet more preferably in a range from about 1.5 to 4.
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Abstract

The present invention relates to a new and environmentally sound process for the manufacturing of a chemical pulp from lignocellulosic material with an integrated recovery system for recovery of pulping chemicals. The process is carried out in several stages involving a pre-treatment stage followed by one or more delignification stages using an alkaline buffer solution comprising alkali metaborate and sodium carbonate as major components.

The alkaline components of the pulping liquor are recovered from a chemicals recovery furnace and at least a portion of the alkali is recycled and used for delignification without any prior reactions with lime or calcium compounds for generation of alkali hydroxide. A quinone based delignification catalyst may be added to be present during delignification. In a preferred embodiment of the invention the quinone pulping catalyst is added prior to alkaline delignification, said delignification conducted in the substantial absence of sulphide.

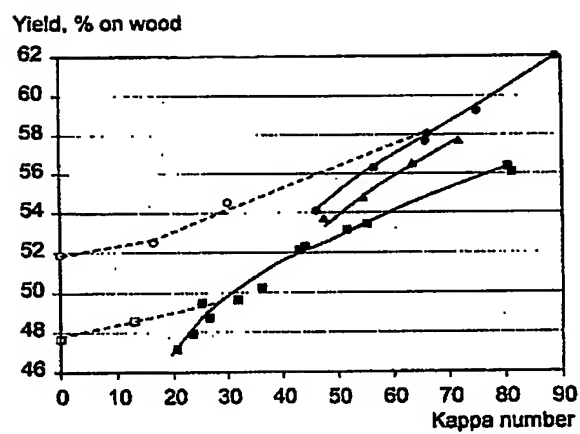


Fig. 1

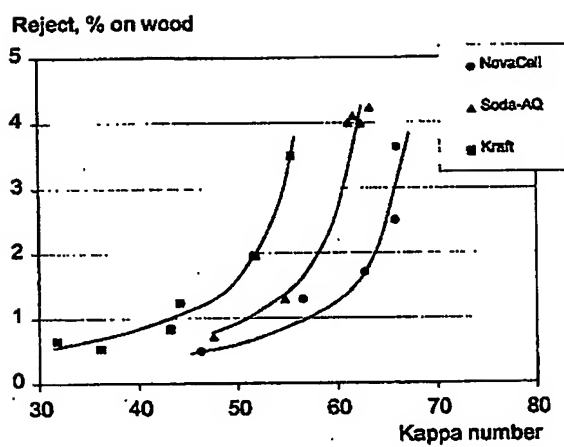


Fig. 2